SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF RETAINED PYRIDINE FROM
PYRIDINE EXTRACTS

Barbara F. Smith, Clifford G. Venier, Thomas G. Squires,
Juliana C. Shei, and Jacqueline D. Hunt

Ames Laboratory*, Iowa State University, Ames, Iowa 50011

INTRODUCTION

Solvent extraction of coal is quite attractive to the organic chemist as a means of obtaining a coal model which (a) is directly related to coal, (b) is devoid of complicating mineral matter, and (c) is soluble in at least one solvent. Pyridine is one of the best common solvents for coals with a carbon content of less than 90% (1,2). It has been used extensively for bituminous coals, typically affording extraction yields of 15-30%.

Unfortunately, the use of pyridine as an extractant suffers the major disadvantage that significant amounts of pyridine are retained in coal extracts. Collins, et. al.(3) show that while only 0.24% of the extract weight is irreversibly bound pyridine, fully 11.8% by weight of pyridine cannot be removed under high vacuum (0.133 Pa) in 48 hours, and repeated benzene washing only lowers the pyridine content to 8.85% in an Illinois No. 6 coal extract.

Having qualitatively observed that at least some of the retained pyridine was removed from coal extracts by supercritical carbon dioxide ($SC-CO_2$), we proceeded to test the feasibility of $SC-CO_2$ extraction as a means of preparing pyridine free coal extracts.

EXPERIMENTAL

Supercritical CO_2 extraction: Pyridine extract ($\sim$1g) was placed in a 15x0.4 cm. stainless steel column containing 5μm frits on either end and 300 μl. of water was added to the extract. The column was maintained at 40°C (the critical temperature of CO_2 is 31.3°C); the precolumn CO_2 pressure was 112 atm (11.4 MPa); a pressure drop of 12 atm (1.2 MPa) was measured across the column; and an exit flow rate of approximately one ml/sec. (atmospheric pressure) was maintained for 4 hours. A spiral glass tube connected to the exit valve collected any non-volatile material that was removed by CO_2 from the coal extract.

Extraction of coal with pyridine: Extracts were obtained by ultrasonically
mixing coal with five times its weight of pyridine for 30 minutes at room temperature
with a Branson Sonifier 350 (20 kHz with an output power of 350 electrical watts to
the converter) (4); filtering the mixture through a 0.5μm Teflon millipore pad;
concentrating the filtrate on a rotary evaporator and freeze drying the concentrate
with three times its volume of benzene overnight at a pressure of 1.33 Pa (5).
Oxygen was excluded at all times.

RESULTS AND DISCUSSION

Figure 1 shows the difference spectrum generated by subtracting the infrared
spectrum of the CO_2-washed extract from that of the unwashed pyridine extract of
Western Kentucky #9 coal from the Ames Coal Library. The sharp spectrum standing out
above the background is unambiguously that of pyridine (see Table 1), confirming that
the major difference before and after the CO_2 washing is the amount of pyridine in
the sample. A small amount of an oil which is primarily aliphatic in nature was also
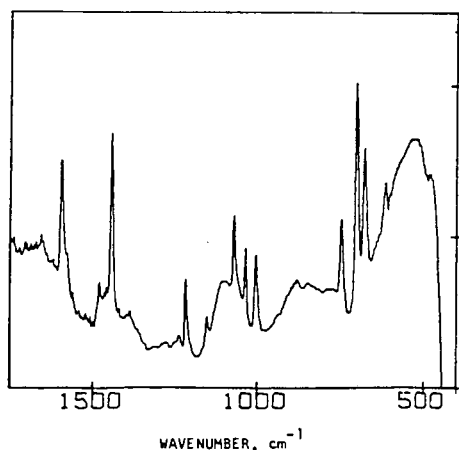recovered in the eluent from the washing (see Table 3 for weights).

WAVENUMBER, cm^{-1}

Figure 1. Difference Infrared Spectrum of the
Pyridine Extract of a Western Kentucky No. 9
Coal Before and Ater Washing with Supercritical
Carbon Dioxide.

Table 1. Infrared Absorption Maxima (cm^{-1})

Difference Spectrum (Fig. 1)	Pyridine[a]
1593	1583, 1572
1479	1482
1442	1439
1213	1218
1148	1148
1067	1068
1034	1030
1003	992
748	749
703	700
679	---
616	605

[a]A. R. Katritzky and P. J. Taylor, "Infrared
Spectroscopy of Heterocycles," in Physical
Methods in Heterocyclic Chemistry, vol. 4,
Academic Press, New York, NY, 1971, pp. 266-
434.

85

The chemical analyses of coals, extracts and CO_2-washed extracts are in Table 2. Note that the amount of nitrogen in the sample is an important indication of excess pyridine. Assuming that pyridine is the only nitrogen containing compound which would be lost in the carbon dioxide washing, the retained pyridine can be expressed as equation 1.

$$\%\text{pyridine} = \frac{\%N_{obs} - \%N_{ext}}{\%N_{pyr} - \%N_{ext}} \times 100 \qquad\qquad 1)$$

where $\%N_{obs}$ is the nitrogen found, $\%N_{pyr}$ is the nitrogen content of pyridine (17.72%) and $\%N_{ext}$ is the nitrogen content of the pyridine free extract

However, the value of the numerator in equation 1 is very sensitive to the exact choice of $\%N_{ext}$ and this means that the % pyridine cannot be accurately calculated or used as a reliable basis for comparing samples. By expressing the difference in pyridine levels between the extract before and after CO_2 washing as $\Delta\%$ pyridine, we obtain equation 2, which is relatively independent of the $\%N_{ext}$.

$$\Delta\% \text{ pyridine} = \frac{\%N_{obs}^{before} - \%N_{obs}^{after}}{\%N_{pyr} - \%N_{ext}} \times 100 \qquad\qquad 2)$$

Table 3 shows the values for $\Delta\%$ pyridine, the weight percent of a small amount of a highly aliphatic oil which was co-extracted, and the gravimetrically measured weight losses due to the extraction with CO_2. The amount of pyridine removed by the carbon dioxide extraction (8.5 to 10.2%) is in good agreement with Collins' finding that 8.8 to 11.6% pyridine is retained by the extract but not irreversibly bound to it.

The removal of pyridine from the solid extract is analogous to the selective extraction of alkaloids from plant materials with supercritical $CO_2(6)$. In many cases water is as essential for the extraction of nitrogenous bases (e.g. caffeine from coffee beans(7), nicotine from tobacco leaves(8)), as it is for the extraction of pyridine from coal extracts. When dry coal extracts are washed with supercritical CO_2, even for extended periods of time, infrared spectra show that pyridine has been only partially removed.

One intriguing possibility is the pyridine removed under dry conditions is that pyridine which can be removed by benzene washing and that wet carbon dioxide removes the more tightly bound non-extractable pyridine.

TABLE 2. Chemical Analyses of Samples[a]

| | ILLINOIS #6 | | | | WESTERN KENTUCKY #9 | | | |
| | Coal[b] | Extract | CO$_2$-Washed Extracts | | Coal[b] | Extract | CO$_2$-Washed Extracts | |
			Exp. 1	Exp. 2			Exp. 1	Exp. 2
C	78.82	80.93	79.02	79.30	82.39	81.86	80.97	80.99
H	5.50	6.45	6.19	6.08	5.83	6.48	6.33	6.27
N	1.59	2.91	1.52	1.53	1.91	3.67	2.22	2.09
S$_{org}$	2.29	2.08	2.07	1.98	2.37	1.58	1.89	1.80

[a] Analyses by Galbraith Laboratory, Knoxville, TN.

[b] Dmmf[c]; % mineral matter = 1.13 (%Ash) + 0.47 (%S$_{pyr}$) + 0.5(%Cl), and

$\%C_{org} = \%C_{dry} - 0.014(\%Ash) - 0.0055(\%S_{pyr})$, and

$\%H_{org} = \%H_{dry} - 0.013(\%Ash) + 0.02(\%S_{pyr})$.

[c] Given, P. H. and Yarzab, R. F., in Karr, C., Jr., ed., Analytical Methods for Coal and Coal Products, Volume II, Academic Press, New York, NY, 1978, Chapter 20.

TABLE 3. Results of Carbon Dioxide Extraction of Pyridine Extract

Source Coal	Δ% Pyridine[a]	% Oil Extracted	% Weight Loss[b]
Ill. No. 6 (1)	8.6	2.3	11.2
Ill. No. 6 (2)	8.5	2.3	12.2
W. Kent. No. 9 (1)	9.3	0.2	13.3
W. Kent. No. 9 (2)	10.2	0.6	13.9

[a] Calculated according to equation 2, assuming $\%N_{ext}$ = 1.5 for Ill. No. 6 and 2.0 for W. Kent. No. 9.

[b] Based on weight of sample before and after CO_2 extraction.

The effectiveness of supercritical carbon dioxide for removing pyridine may be due to one or all of the following explanations:

(1) Supercritical carbon dioxide can penetrate the interior of the solid extract more effectively than liquid benzene;

(2) Carbon dioxide has the ability to displace pyridine whereas benzene cannot;

(3) The extracting agent is actually carbonic acid, not carbon dioxide, and the process is an acid-base extraction.

Our results suggest that the carbonic acid extraction of the basic pyridine is the most satisfying explanation.

REFERENCES

1. Van Krevelen, D. W., Coal, Elsevier Publishing Co., N.Y. 1961, Ch. X, p. 177-200.

2. Wender, I.; Heredy, J. A.; Neuworth, M. B.; Dryden, I.G.C., "Chemical Reactions and the Constitution of Coal" in Chemistry of Coal Utilization, Second Supplementary Volume, M. A. Elliot, ed., Wiley, New York, N. Y., 1981, Ch. 8, p. 425-521.

3. Collins, C. J.; Hagaman, E. W.; Jones, R. M.; Raaen, V. F., Fuel 1981, 60, 359.

4. For discussion of the effects of ultrasonic irradiation on the dissolution of coal, see Kessler, T.; Friedel, R. A.; Sharkey, A. G. Jr., J. Appl. Chem. 1970, 20, 245.

5. Schweighardt, F. K.; Retcofsky, H. L., private communication to F. K. Schweighardt, as quoted on page 199 of Sharkey, A. G., Jr.; McCartney, J. T., "Physical Properties of Coal and its Products," in Chemistry of Coal Utilization, Second Supplementary Volume, Elliott, M. A., ed., Wiley, New York, 1981.

6. Stahl, E.; Schilz, W.; Shutz, E.; Willing, E., Angew. Chem. Int. Ed. Engl. 1978, 17, 731.

7. Zosel, K., Angew. Chem. Int. Ed. Engl. 1978, 17, 702.

8. Hubert, P.; Vitzthum, O.G., Angew. Chem. Int. Ed. Engl. 1978, 17, 710.

REACTION-INDUCED TEMPERATURE DEVIATIONS DURING
COAL DEVOLATILIZATION IN A HEATED GRID

J. D. Freihaut, M. F. Zabielski and D. J. Seery

United Technologies Research Center
East Hartford, CT   06118

INTRODUCTION

Previous investigations in this laboratory using a heated grid apparatus have indicated:

1. Tar yields and the thermal sensitivity of tar yields obtained in primary (pressure $\leq 10^{-2}$ torr, disperse phase of particles ≤ 100 µm) devolatilization conditions are distinguishing characteristics of the devolatilization behavior of coal (1).

2. The evolution of coal nitrogen reflects the evolution of coal mass as char, tar or light gas during primary devolatilization. Via coupling to the tar yield, the evolution of coal nitrogen becomes a distinguishing feature of primary devolatilization (2).

3. Increasing the thermal drive (simultaneously varying apparent heating rate and final temperature) did little to alter the total volatile yield but did alter the distribution of volatiles. The most significant changes observed with variations in apparent heating rates from 10^2 C/sec to 10^3/sec and final temperatures of 600 C and above related to the tar fraction of the volatiles yield (1,2).

A major limitation of the experimental design of these previous experiments was the coupling between the heating rate and final temperature. In addition, no effort was made to determine if the devolatilization process itself significantly influences the temperature history of the sample. To gain further insight into the primary devolatilization process, particularly with respect to the tar yields, a new control circuit was designed to permit any heating rate from 800 C/sec to 4×10^3 C/sec to any final temperature in the 300 to 1100 C range. With this circuit, the effects of sample characteristics on local heating of the grid were examined to assess the influence of devolatilization on programmed heating rates.

In addition to gaining further insight into the tar evolution process it is desirable to address such questions as:

1. Can the primary devolatilization process significantly alter the temperature history of the devolatilizing coal mass?

2. Do coals of varying rank characteristics show the same thermal requirement characteristics when subjected to the same rapid heating conditions?